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ORIGINAL ARTICLE

Evaluation of organochlorinated pesticide (OCP) residues in soil, sediment and water from the Msunduzi River in South Africa

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Abstract
Organochlorinated pesticide (OCP) concentrations were evaluated in sediment, soil and surface water of the Msunduzi River as well as the influent, effluent and biosolids from the Darvill wastewater treatment plant (WWTP) of Pietermaritzburg, South Africa. Samples were extracted with dichloromethane using an ultra-sonication method, and cleaned up using multi-layered silica gel and analysed using gas chromatography-mass spectrometry. The results showed that all 13 selected OCPs were detected in all the environmental media as well as in the wastewater treatment plant samples. The results revealed that the OCP concentrations along the sites varied based on the anthropogenic activities of the area. The influent of the Darvill WWTP and Du Toit (DUT) site were found to be the most polluted sites. The results from the winter sampling showed highest concentrations of OCPs compared to the spring season. Sediment was found to contain significant amounts of all the selected OCPs with water samples containing the lowest concentrations for both winter and spring seasons. Among the OCPs evaluated, dichlorodiphenyltrichloroethane (DDT) and its metabolites were predominant in all.

Keywords Organochlorinated pesticides · Msunduzi River · Wastewater treatment plant · Winter and spring seasons

Introduction

Organochlorine pesticides

Organochlorinated pesticides (OCPs) are important classes of POPs listed under the Stockholm convention's dirty dozen list, which are a concern to the local and international communities (Bouwman 2004; Covacia et al. 2005; Wurl and Obbard 2005). OCPs are predominantly used in agrochemical industries most especially in agriculture as pesticides, fungicides and insecticides for vector control and an increase demand for quality and quantity of food products. (Eqani et al. 2011; Ansara-Ross et al. 2012). Although, the production and usage of most OCPs has been banned worldwide their usage continues illegally in most developing countries most especially in many parts of African countries. South Africa has been reported to be the largest market for pesticides in sub-Saharan Africa with approximately 60% of pesticides sold across the African continent (Dinham 1993; Bouwman 2003; Naidoo and Buckley 2003). Similarly, some of these OCPs have been formulated, registered and sold commercially under different trade names to avoid suspicious usage, such as DDD was produced and sold by another name "Rothane" (Van Dyk et al. 1982; Nel et al. 2000; Meinhardt 2003, 2008). Soil and sediment are the main reservoirs for OCP accumulation over time (Nieuwoudt et al. 2009). Due to the persistence, long half-life, slow rate of degradation the ease of accumulation in soil and sediment, as well as their long and wide range of transportation some levels OCPs have been reported in different environmental matrices globally most especially in soils and sediments (Aydin and Yurdun 1999). Zhou et al. (2006) investigated the levels of 13 OCPs in surface water and sediments from Qiantang River in East China. The authors reported that significant amounts of OCPs were still present in the environmental matrices investigated with total OCP concentrations

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in surface water and sediments $7.68 \times 10^{-3} - 2.694 \times 10^{-1}$ µg L^{-1} and 23.11–316.5 µg kg^{-1}-dry (dw), respectively. Similarly, some levels of OCP concentrations were reported by Tolosa et al. (1995) in surface sediment of Cienfuegos Bay, Cuba. The result revealed that surface sediment contained about 0.26–5.63 µg kg^{-1} of total DDT while significant amounts of HCB concentrations of 0.015–3.50 µg kg^{-1} were reported. Distribution and ecological risk of OCPs in surface sediments collected from the Bizerte Lagoon, Tunisia were investigated by Barhoumi et al. (2014). The total DDT and HCB reported were 0.3–11.5 µg kg^{-1} and 0.6–2.5 µg kg^{-1}, respectively. Okoya et al. (2013) also reported some level of OCP residues in sediments and waters from cocoa producing areas of Ondo State, Southwestern Nigeria. The authors reported that, sediments samples contained significant amounts of cis-chlordane, α- endosulfan, *p,p*-DDE and dieldrin such as 30–6990 µg kg^{-1}; 30–6990 µg kg^{-1} 80–19,040 µg kg^{-1} and 10–7620 µg kg^{-1}, respectively. OCP levels were reported to be significantly higher ($p < 0.05$) during the dry season compared to the wet season among the selected rivers. In addition, Sibali et al. 2008 detected some OCP concentrations in sediment and surface water samples collected along 7 sampling points within the Jukskei River catchment area in Gauteng, South Africa. The authors noted that, the amount of OCPs found in sediment samples was much higher for δ-HCH (266 ± 0.01 µg kg^{-1}) and 2.2 $914 \times 10^{7} \pm 2.85$ µg kg^{-1} dw for *o,p*-DDE compared to filtered water samples of 0.895 ± 0.01 ng mL^{-1} for γ-HCH and 9 089 ± 0.08 ng mL^{-1} for heptachlor. There is limited information on the levels and distributions of OCPs in South Africa most especially the rivers in KwaZulu-Natal. Previous studies have focused on inorganic pollutants and the few studies done on organic pollutants are outdated. Therefore, there is a need for new research to be conducted on the presence of OCPs in this area and its entry into the Msunduzi River, which is the main water source in this area. The objectives of the present study were to investigate the presence and concentration levels of selected OCP residues such as, hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), heptachlor, aldrin, *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT, *p,p*-DDT, dieldrin, endrin and mirex in sediment, soil and surface water of the Msunduzi River (catchment area) as well as samples from Darvill waste water treatment plant during winter and spring seasons. Figure 1 shows the structures of the selected OCPs investigated in this study.

Materials and methods

The study area was the Msunduzi River and Darvill WWTP both in Pietermaritzburg catchment area, KwaZulu-Natal, South Africa. The Msunduzi River catchment is popularly known by its anglicised name, the Dusi River, located in the uMgungundlovu district municipality, which covers an area of 901 km^2 and has a length of approximately 21.55 km. The catchment is distributed within the Northwestern extremity at an altitude of ± 1520 m above sea level near Ka-Nzakane and at an altitude of ± 1390 m

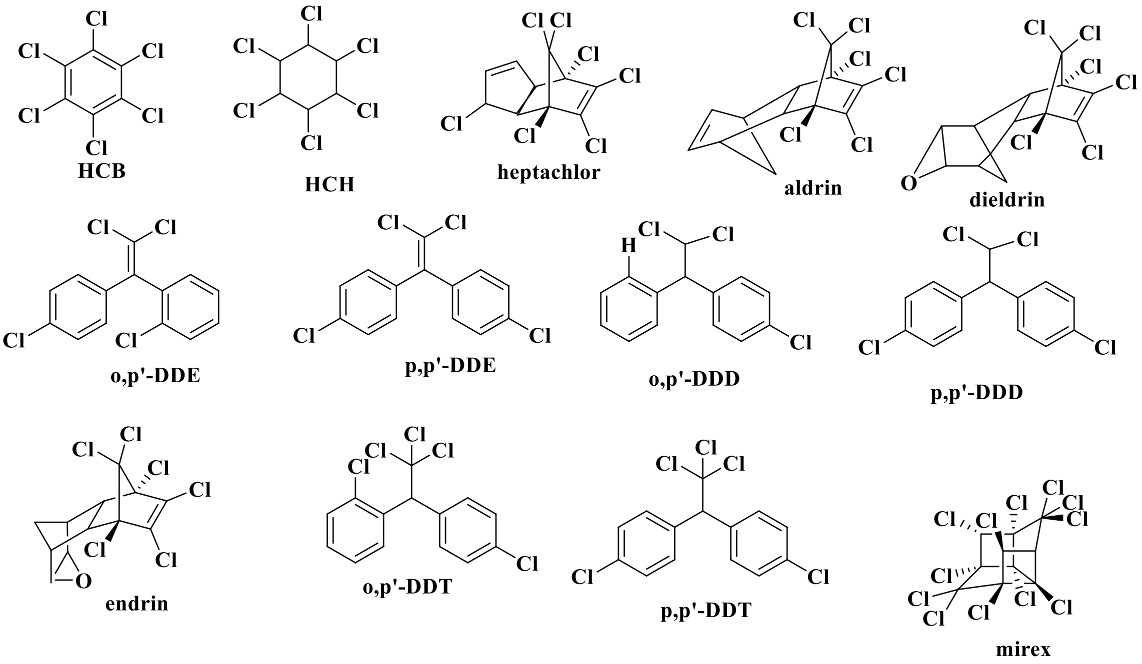

Fig. 1 Structures of selected organochlorine pesticides

above sea level near Mafunze in the Southwest, the perennial Msunduzi flows 150 km (excluding tributaries) to its confluence with the Umgeni River at an altitude of ± 285 m. The catchment has a topology of mountainous with different hills, lowlands, wetlands, marshes and flat areas. The annual precipitation within the Msunduzi River catchment ranges from 684 to 1186 mm (Gericke et al. 2004). The major land use in the Msunduzi River catchment includes: forest, open spaces, grassland, Central Business District and industrial area, low-density residential, medium-density residential and high-density residential, as well as wetland area. Generally, the amount of residential land (± 189 km^2) is smaller than the amount of grassland (± 276 km^2), reflecting the rural nature of the upper Msunduzi River catchment (Gericke et al. 2004). The Msunduzi River was chosen for this study because it possibly receives effluent from untreated domestic waste from rural areas (sewage), unmanaged municipal waste dumps as well as agricultural drainage, which could be a possible contributing factor to the organic pollution levels in the river. The upper reaches of the river is dammed for hosting the Dusi canoe marathon, the annual national water sport festival; where people could possibly be at risk of exposure to these toxic organic chemical pollutants. Samples were collected between 16th–17th July, and 25th–26th September, 2013 for winter and spring seasons, respectively. The periods were selected to further understand the effect of seasonal variation and distribution of the pollutants in the environment. In South Africa, the seasonal change follows the meteorological pattern of the Southern Hemisphere. The month between June to late August of the year (winter) is characterized with little or no rainfall (low precipitation rate) thereby resulting in low water volume, the weather is relatively cool with low sun intensity. While spring season spans between September to the end of November each year. During this period, the precipitation rate as well as sun intensity are relatively high, resulting in high water levels in the river (higher water volume), with relatively higher evaporation rates as compared to the winter period. There is relatively low infiltration rate with high surface runoff on Msunduzi River catchment due to the impervious nature of the soil, land and natural features such as rock outcrops, canopy interception of vegetation, with high density of clay soil. The Msunduzi River and sampling points were chosen for this study because it is the major source of water to the larger population of the area as well as there are a high number of anthropogenic activities that are suspected sources of contamination. Surface water, sediment, and soil samples were collected starting from downstream of the Henley Dam influent, biosolid and effluent samples were collected from Darvill WWTP while a sample was collected at Nagle Dam on the Umgeni River, which is before the joining of the Msunduzi River with the Umgeni River (Fig. 2).

Reagents and materials

All reagents and chemicals were of HPLC-grade, as well as the thirteen OCPs standards were purchased from Sigma-Aldrich South Africa. They were HCB, HCH, heptachlor, aldrin, *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT, *p,p*-DDT, dieldrin, endrin and mirex. High-purity anhydrous sodium sulfate Gold line (CP) with CAS No. 7757-82-6 was obtained from Associated Chemical Enterprises (ACE) and used as a desiccant throughout the study, while silica gel, grade 634, of 100–200 mesh (0.063–0.2 mm) size, obtained from Merck, was used for both basic and acidic silica gel prepared in the laboratory for the clean-up of the extracts prior to analyses. Reagent-grade sulfuric acid (specific gravity 1.84) obtained from Promark Chemicals was used for acidification.

Sampling and sample treatment

Sample collection

Soil, sediment and water sampling technique employed following a standard method as set out by USEPA (2007). Briefly, sediment samples were collected by scooping 0–10 cm of the sediment from the river bed with a stainless steel spade, while the soil samples were collected at a depth of 0–15 cm on the banks of the river close to the water using a grab sampler and stainless steel auger and stored in glass bottles. Water samples were collected in 2.5 L amber reagent bottles, which were washed with phosphate-free soap (dDyna Chem), rinsed with tap water and distilled water and finally rinsed with HPLC-grade acetone, and *n*-hexane to eliminate both polar and non-polar contaminants prior to sampling. Bottles were rinsed twice with the river water to be sampled, before the water sample was collected. A grab sampling technique was used to collect water samples from a depth of 1–2 cm from the water surface. A 1 mL aliquot of 50% sulfuric acid was added to each of the samples, immediately after collection, to prevent microbial degradation of the samples. The lids of the glass bottles were lined with acetone-pre-washed aluminium foil to prevent possible sample contamination from phthalates, which could leach from the plastic lining of the lid. Samples were kept cool under ice during transportation to the laboratory. Samples were kept at 4 °C prior to extraction to prevent break down and bio-degradation of compounds of interest (Hilscherova et al. 2003). Soil and sediment samples were air-dried in the fume hood for 5 days; the dried samples were sieved with 75 µm, 300 µm, and 450 µm stainless steel sieves and stored in the fridge prior to extraction.

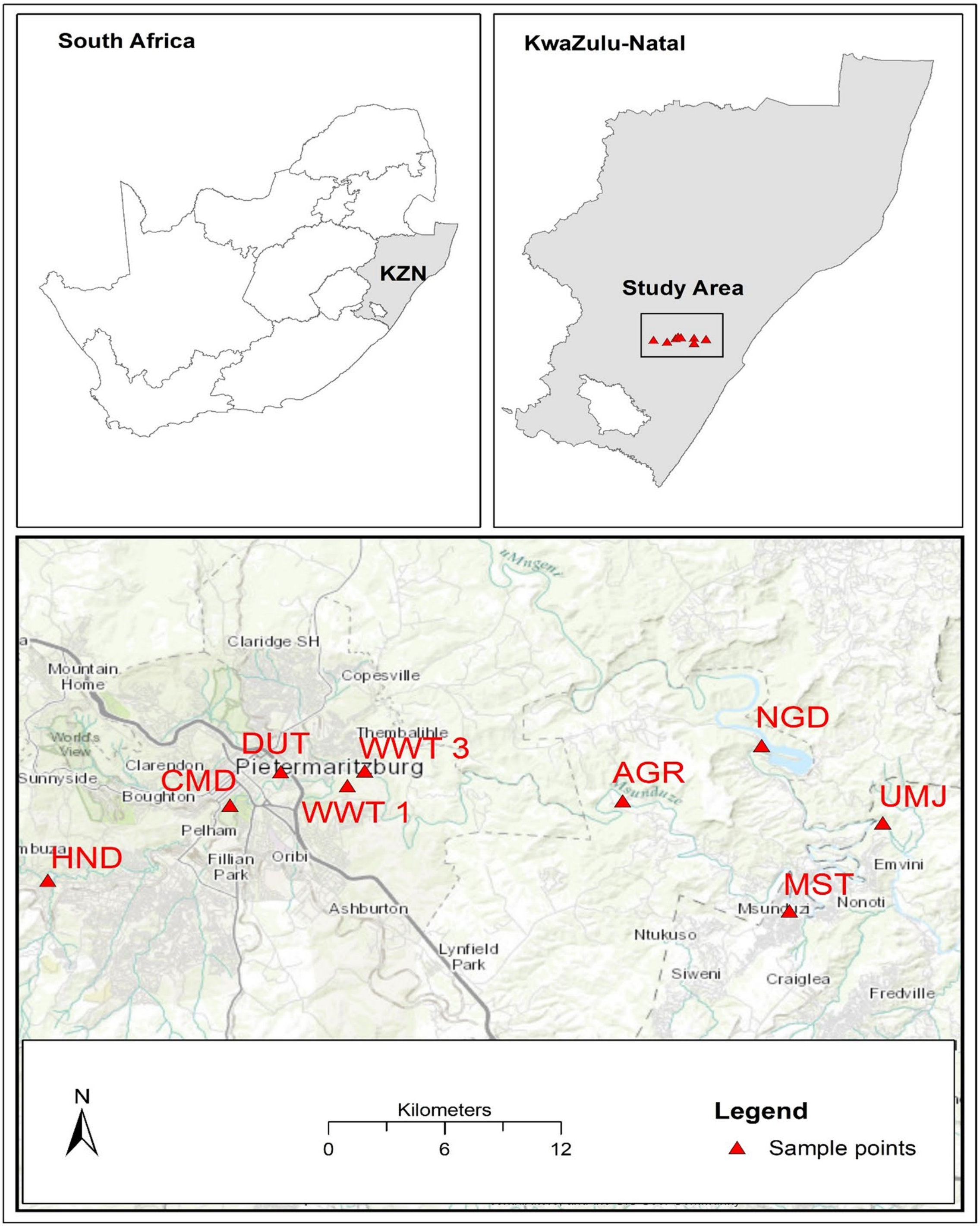

Fig. 2 Sampling sites along the Msunduzi River, South Africa (created using ArcMap10.4 version)

Sample extraction

All the glasswares were baked in the oven at 130 °C, overnight prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use. Soil and sediment samples (20 g dw each) were dried and homogenized and then mixed with 10 g of anhydrous sodium sulfate to remove the excess moisture from the sample. Soil and sediment samples were extracted using an ultrasonication method (USEPA Method 3550C, 1984 revised 2007) with three times 20 mL dichloromethane

(DCM), at 30 °C for 30 min each. Extracts were combined, filtered and concentrated to 2 mL using rotary evaporation.

Water extraction was carried out using a liquid–liquid extraction following USEPA method 3510-C (USEPA 1996a). Liquid–liquid extraction has been reported to offer better results as compared to the solid-phase extraction (SPE) method (Fatoki and Awofolu 2003; Sibali et al. 2008) because it prevents the introduction of phthalate ester interferences that may originate from the housing materials of the cartridges (Fatoki and Awofolu 2003). Briefly, a 500 mL aliquot of water was extracted with three times 40 mL DCM. The extract fractions were combined and concentrated to 2 mL using a rotary evaporator. The wastewater sample was filtered through a vacuum glass funnel, prior to the extraction, to remove suspended particles within the water sample.

Separation (clean-up)

A multi-layer silica gel column was used in this study as recommended by the United States Environmental Protection Agency (USEPA method 1668B 2008) for anthropogenic pollutants. The column was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel; 10 g anhydrous sodium sulfate (Na_2SO_4). The column was pre-eluted with 20 mL *n*-hexane, thereafter the extract was loaded and eluted with a total volume of 50 mL of *n*-hexane:DCM:toluene in the ratio 2.5:1.5:1. The fractions were combined and the volume reduced to 2 mL using rotary evaporation and finally air-dried. Samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45 µm acrodisc filter prior to GC-MS analysis.

GC–MS analysis

Stock solutions of 200 mg L^{-1} of individual standards were prepared by dissolving 0.02 g of the individual OCP standards in 100 mL of dichloromethane and stored in the refrigerator at 4 °C. The OCPs lower working concentrations were prepared by appropriate dilution. Samples were analysed using gas chromatography/mass spectrometry (GC/MS Shimadzu QP-2010 Ultra Japan), using a DB-5MS capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness). Helium was used as the carrier gas with a flow rate of 0.72 $mLmin^{-1}$ and a total flow of 31.8 $mLsec^{-1}$, a linear velocity of 32.2 cm/s at purge flow of 3.0 $mLmin^{-1}$ using splitless mode. The injection and detector temperatures were set at 220 °C and 320 °C, respectively. Oven temperature was set at 150 °C and held for 2 min, raised to 295 °C at 14°C/min and held for a further 2 min. A 1-µL injection volume was used. All the quality control steps were followed. Laboratory blanks for both water and sediment that were subjected to the same analytical procedures as applied to the original samples did not show any significant peaks. Samples were analysed in triplicate. The linear range values (R^2) for all the analytes, LOD and LOQ values are shown in Table 1 Sediment recoveries were determined using the method adopted by McCarty and co-workers for matrix spiked data at 80 $ngmL^{-1}$, while water recoveries were determined by spiking a 0.5 L tap water at 8 ng mL^{-1} (McCarty et al. 2008). Method recoveries were evaluated based on the USEPA standard method 1668B (2008). Average triplicate OCP recoveries for water and sediment ranged between 59–103% and 87–126%, respectively, as shown in Table 1 and are within standard acceptable limits. Routine analysis of blanks with every ten sample sets were carefully

Table 1 Percentage recoveries based on spiked sediment and spiked tap water, R^2 values, limits of detection and quantification of OCPs in water and sediment

OCPs	Percentage recovery		R^2 value ($n=3$)	Limit of detection/limit of quantification			
	Water	Sediment		Sediment/(ng g^{-1})		Water (ng mL^{-1})	
				LOD	LOQ	LOD	LOQ
HCB	83	126	0.9980	0.0073	0.0220	0.0006	0.0018
HCH	71	117	0.9962	0.0030	0.0092	0.0002	0.0007
Heptachlor	59	89	0.9948	0.0043	0.0131	0.0003	0.0010
Aldrin	68	98	0.9966	0.0042	0.0128	0.0003	0.0010
o,p-DDE	65	92	0.9918	0.0030	0.0090	0.0002	0.0007
p,p-DDE	67	105	0.9991	0.0021	0.0062	0.0002	0.0005
o,p-DDD	68	115	0.9930	0.0091	0.0275	0.0007	0.0022
Dieldrin	60	87	0.9981	0.0054	0.0163	0.0004	0.0013
Endrin	78	106	0.9935	0.0018	0.0055	0.0001	0.0004
p,p-DDD	67	122	0.9907	0.0070	0.0213	0.0006	0.0017
o,p-DDT	100	104	0.9982	0.0026	0.0080	0.0002	0.0006
p,p-DDT	78	110	0.9964	0.0080	0.0243	0.0006	0.0019
Mirex	103	92	0.9992	0.0015	0.0046	0.0001	0.0004

monitored to determine the possibility of any interferences from the column. Standards were run intermittently between samples to monitor changes in the instrument's sensitivity. Sediment and water sample extracts were spiked with the mixed OCPs standards at 0.50 ng g^{-1} and 0.25 ng mL^{-1}, respectively, and their concentrations were determined. An external calibration method was used for the quantification of seven OCPs together with 6 DDT metabolites based on the peak areas of the targeted compounds. Analytes were identified by comparing their retention times with those of the targeted OCP standards.

Results and discussion

The OCP concentrations in sediments samples along the selected sites for both winter and spring seasons were presented in Fig. 3a and b, respectively. OCPs concentrations during the winter period were found to be slightly higher in sediment compared to that of the spring season. This observation could be attributed to the fact that low temperature (Table 2) during the winter season could possibly discourage the volatilization of the pollutants. A low aqueous solution temperature generally favoured hydrophobic organic pollutants such as OCPs with higher degree of chlorination by discouraging their aqueous solubility thereby encourage the pollutants to bind to the sediments interlayers. Concentrations of organic pollutants in environmental media are known to be dependent

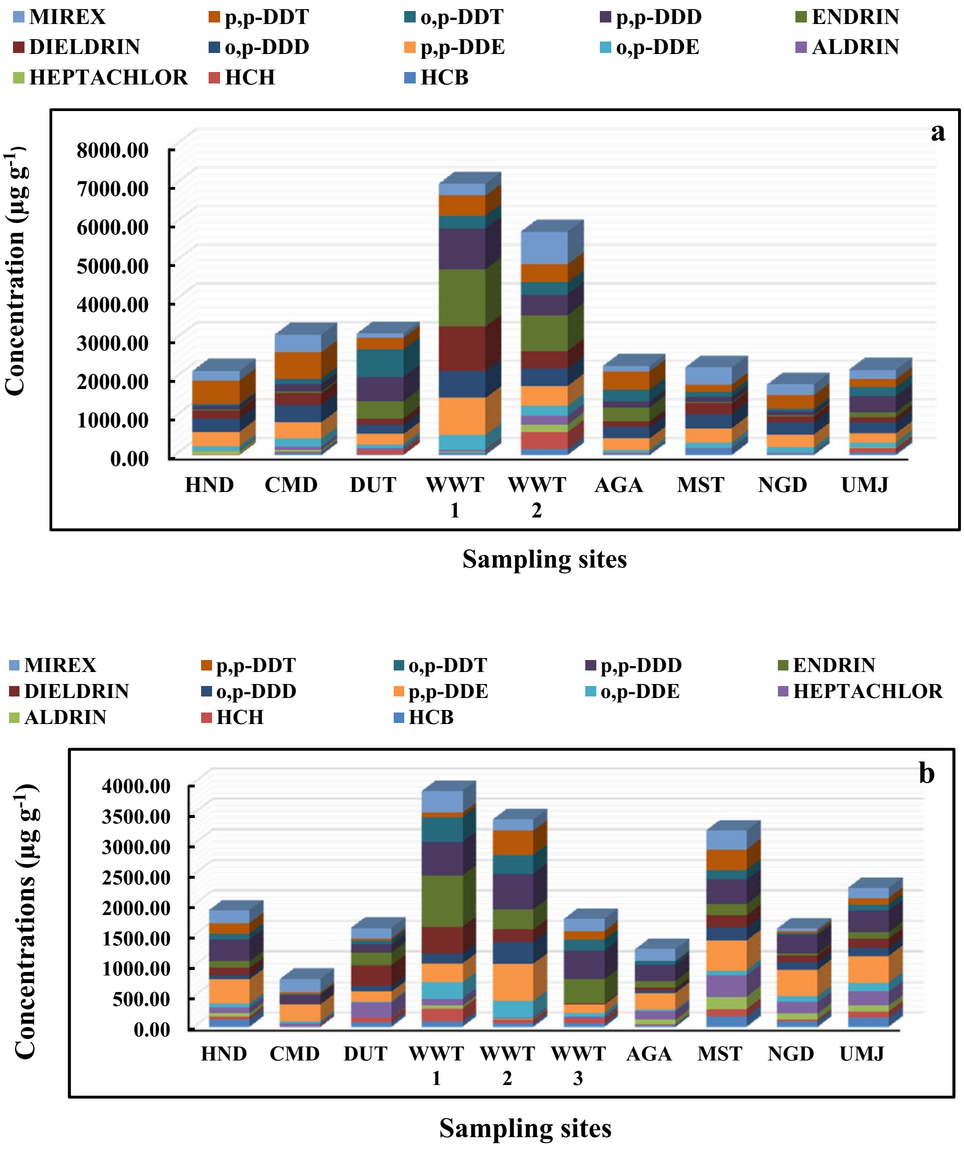

Fig. 3 Concentrations of OCPs in sediments during **a** winter and **b** spring seasons

Table 2 Sampling coordinates, physicochemical parameters and sampling site description

Site name	Location	Physicochemical parameters of water				Land use category	Description of the sampling site
		pH		Temperature (°C)			
		Winter	Spring	Winter	Spring		
HND	29° 38′51″S 30° 17′32″E	6.21	7.52	14	19	Urban	Dense urban area of Edendale with domestic, agricultural activities. Sampling site was on the river but upstream of Henley Dam
CMD	29° 36′47″S 30° 22′36″E	5.15	8.05	21	21	Urban/commercial	Dense urban area of Pietermaritzburg, downstream of Camps drift area with domestic and commercial activities
DUT	29° 35′52″S 30° 24′01″E	7.20	7.49	15	18	Urban/commercial	Dense urban area of Pietermaritzburg. The site was observed to be characterized with some illegal dumping of waste. Also, confluence with Bayne's Spruit River, which passes through informal settlements
WWT 1	29° 36′15″S 30° 25′52″E	5.31	7.24	19	22	Urban/rural	Residential areas of Hayfields and Sobantu. Received influent of various wastes from the city of Pietermaritzburg and adjacent to Sobantu landfill dump site
WWT 2	29° 36′15″S 30° 25′52″E	5.54	7.85	19	22	Rural	Effluent of treated waste from the wastewater treatment plant
WWT 3	29° 36′15″S 30° 25′52″E	–	7.70	–	22	Rural	Effluent of treated waste discharged, agricultural activities and close to Sobantu landfill dump site
AGR	29° 36′40″S 30° 33′32″E	5.12	8.72	14	24	Rural	Rural settlement with agricultural activities such as sugar cane plantations, homestead agricultural activities, and pasture production, commercial forestry as well as subsistence farming
MST	29° 39′40″S 30° 38′10″E	4.77	8.92	15	26	Urban, industrial/commercial	Dense urban settlement with potential impact from the aluminium smelters, textile and footwear factories as well as food-processing plants. Also, impact of informal settlement of Vulindlela situated southwest of the town, and close proximity of open illegal dumping of household waste on the river
NGD	29° 35′08.42″S 30° 37′23.94″E	5.56	8.87	15	21	Rural	The dam is on Umgeni River, which serves as the main water supply to households and local industries as well as agricultural irrigation water supply for the surrounding communities
UMJ	29° 37′16″S 30° 40′46″E	5.07	7.60	15	25	Rural	A few metres away from Msunduzi–Umgeni River confluence point located along the informal rural settlement. The river also has some tributaries at upstream, which receives agricultural and surface water runoff

HND Henley D outlet; *CMD* camps drift, *DUT* Du Toit, *WWT1* Darvill wastewater treatment plant 1 (inlet), *WWT2* Darvill wastewater treatment plant 2 (after chlorination), *WWT3* Darvill wastewater treatment plant 3 (discharge), *AGA* agricultural area, *MST* Msunduzi Town, *NGD* Nagle Dam, *UMJ* Umgeni, Msunduzi River joining point

on adsorption–desorption from sediment based on temperature changes (Zhou et al. 2006; Cheng et al. 2007). Another important parameter that could possibly favour slightly higher concentrations of these pollutants in sediments during the winter period is low solution pH. Water pH was slightly acidic during the winter period compared to a more alkaline solution as observed for spring season (Table 2). The implication could be that soil organic matter is more protonated at low pH during the winter period which could possibly make sediment more hydrophobic thereby encouraging more hydrophobic OCPs to bind to the sediments favourably compared to the deprotonated sediments/water system during the spring period. In addition, the low water flow due to the low rainfall experienced during winter also contributes to the high concentrations of OCPs found during this sampling season.

Distribution and pollution levels of the OCPs in different media along the river are shown in the Fig. 3a and b and Table 3a and b, respectively. Among the studied sites, wastewater treatment plant 1 (influent) (WWT1) was found to be the most polluted site for both sediment and water analysed during the winter and spring seasons. The significant amounts of OCPs detected at WWT 1 could be attributed to possible combinations of untreated wastewater from industrial effluent as well as domestic sewage. In addition, the low concentrations found at WWT 3 could be due to the waste treatment plant process not completely removing these pollutants during the various treatment stages. Previous studies have also shown high pollution load due to similar sources of effluent (Zhang et al. 2003; Zhou et al. 2006).

A high concentration of OCP residues in all sample media for both seasons was also recorded at the Umgeni–Msunduzi joining point (UMJ) (Figs. 3a and b, 4a and b; Table 3a and b). The high concentration is probably due to the combined total pollutants received from both the Umgeni River and the Msunduzi River. In addition, there are also some rural farming activities close to this site, which could be a point source for OCPs at this site. Msunduzi town (MST), Du Toit (DUT) and Henley dam outlet (HND) sampling sites also contained higher OCP concentrations. There is no specific information available about the sources of these pollutants in the area, but pollution rate at MST and HND sites could possibly be due to the runoff from agriculture because these sites are located in rural areas with agriculture as a major activity. The presence of OCPs at these sites could also be from previous use as vector controls prior to their banning. Similar studies by Minh and co-workers showed that OCPs are able to remain in the environment long after their use thus confirming their persistence (Minh et al. 2004). Du Toit is located in the city centre of Pietermaritzburg and the concentrations of OCPs in this area could possibly be as a result of transportation of OCPs from agricultural activities upstream that are taken along with the flow of the river and deposited downstream. There are also a few small tributaries that flow into the Msunduzi River bringing with it possible sources of OCPs from the surrounding rural agricultural areas. Other sites with relatively high concentrations of OCPs were the agricultural area (AGR), Nagle Dam (NGD), WWT 2 and Camps drift (CMD). Site AGR is located in a rural area with a lot of farming activities where OCPs could possibly be entering into the river ecosystem through surface runoff from surrounding crops. Nagle dam is on the Umgeni River which is the main river in the province of KwaZulu-Natal. There are a number of tributaries which eventually make their way to Nagle dam. There is also some minor farming activity in the surrounding area of Nagle dam, which may contribute to run-offs into the dam. Wastewater treatment (WWT 2) refers to the effluent after chlorination from the Darvill wastewater treatment plant. This site was found to contain some level of OCP pollutants, which could possibly be from insufficient removal of the selected organochlorinated pesticides from the treatment plant itself. Research has shown that water treatment plants generally do not remove pesticides (Fatoki and Awofolu 2003). Camps drift is a popular site for the annual Dusi festival. The presence of the OCPs at this site could not be categorically ascertained, however because of trans boundary effects and long range of transportation OCPs could be transported from the upper course of the river to this sampling site (UNEP 2001).

The OCP concentration levels in sediment, soil and surface water samples during winter and spring seasons are shown in Figs. 3a and b, 4a and b and Table 3a and b, respectively. Among the OCPs evaluated DDT and its metabolites were predominant across the sampling sites in both seasons for sediment, soil and water samples. Technical DDT (DDT mixtures) in general contain 75% *p,p*-DDT, 15% *o,p*-DDT, 5% *p,p*-DDE, and < 5% others (Metcarf 1973; Bopp et al. 1982). Possible pollution sources of DDT can be assessed using relative total concentrations of DDTs together with its biological metabolites such as DDD and DDE, which is an indicative index of pollution assessment. DDT is susceptible to degradation under aerobic conditions to DDE and under anaerobic condition to DDD (Bossi et al. 1992). A ratio of DDE + DDD/DDTs > 0.5 indicates long-term weathering while a ratio of DDD/DDE > unity (1), indicates that the sediments were dominated by DDD which results from anaerobic degradation of DDT (Hitch and Day 1992; Doong et al. 2002a, b). The ratio of DDD/DDE was determined to be 1.28 and 1.04; 1.12 and 0.56 in sediment and soil for winter and spring seasons, respectively. They were greater than unity except for soil samples during the spring season, which indicated that both the sediment and soil of Msunduzi River are both dominated by *p,p*-DDD, a product of anaerobic degradation of *p,p*-DDT (Zhou et al. 2006). The ratios of (DDE + DDD)/DDTs in both surface sediment and soil were 0.67 and 0.77, and 0.64 and 0.58 in both winter and spring season were also greater than 0.5. This result revealed that DDT metabolite contamination in soils and sediments of the Msunduzi River may be as a result of long-term weathering of DDTs along river and retained by anaerobic conditions within the sediment and soil in the river. To assess the trend of DDT sources in water, the ratio of DDE/ΣDDTs and DDD/ΣDDTs were evaluated and values of 1.56 and 2.90, and 1.61 and 2.62 were obtained for both winter and spring seasons, respectively. The values were greater than unity in water, which is an indication that DDT metabolite contamination may be as a result of aged long weathering of DDT in the Msunduzi River. Mirex was also found to be more prevalent in the environmental media investigated during both seasons. Mirex showed a significant

Table 3 OCP concentrations in water samples (μg mL^{-1}) along the Msunduzi River during (a) winter and (b) spring seasons

Site code (a)	HCB	HCH	HEPTA-CHLOR	ALDRIN	*o,p*-DDE	*p,p*-DDE	*o,p*-DDD	DIELDRIN	ENDRIN	*p,p*-DDD	*o,p*-DDT	*p,p*-DDT	MIREX
HND	3.31 ± 0.86	8.77 ± 1.15	2.55 ± 1.14	3.72 ± 0.8	9.17 ± 0.3	14.36 ± 0.29	16.36 ± 0.23	8.39 ± 0.19	2.95 ± 1.32	6.71 ± 1.21	1.94 ± 2.16	13.24 ± 0.23	16.79 ± 0.27
CMD	0.76 ± 0.02	11.3 ± 0.5	6.42 ± 0.31	7.71 ± 0.27	6.73 ± 0.32	12.6 ± 0.44	14.24 ± 0.05	6.54 ± 0.28	10.15 ± 0.26	12.35 ± 0.96	7.76 ± 1.5	13.53 ± 0.31	24.98 ± 0.41
DUT	6.34 ± 0.16	36.29 ± 1.57	0.73 ± 0.14	0.55 ± 0.84	12.4 ± 0.66	18.85 ± 0.37	15.77 ± 0.32	12 ± 0.2	16.96 ± 0.65	25.19 ± 0.11	10.11 ± 0.9	5.23 ± 0.25	37.00 ± 0.16
WWT 1	1.54 ± 0.9	12.71 ± 1.99	3.1 ± 0.8	4.29 ± 0.6	8.24 ± 0.17	16.76 ± 0.18	16.23 ± 0.21	9.51 ± 0.15	0.56 ± 0.86	4.37 ± 0.13	0.85 ± 0.68	7.53 ± 0.00	16.17 ± 0.29
WWT 2	3.82 ± 1.67	27.87 ± 0.63	8.8 ± 0.46	10.16 ± 0.41	14.04 ± 0.68	27.5 ± 1.19	13.59 ± 0.37	13.5 ± 0.11	11.17 ± 0.93	28.87 ± 0.48	7.21 ± 0.4	11.46 ± 0.5	29.97 ± 0.89
AGA	1.73 ± 0.49	17.63 ± 0.66	0.06 ± 1.86	1.89 ± 2.16	7.48 ± 0.47	15.06 ± 0.51	15.14 ± 0.43	8.14 ± 0.64	0.37 ± 1.31	2.93 ± 1.55	0.98 ± 0.24	2.09 ± 0.52	12.08 ± 1.33
MST	0.3 ± 0.15	15.84 ± 0.17	0.9 ± 0.21	1.03 ± 2.5	5.56 ± 0.05	10.89 ± 0.11	11.46 ± 0.04	5.3 ± 0.2	0.73 ± 0.33	2.01 ± 0.82	0.89 ± 1.08	15.5 ± 0.91	10.97 ± 0.5
NGD	2.09 ± 0.14	38.59 ± 0.38	4.58 ± 0.21	5.82 ± 0.17	7.27 ± 0.03	13.24 ± 0.02	13.8 ± 0.04	8.65 ± 0.02	26.05 ± 0.37	7.47 ± 0.07	1.97 ± 0.37	19.95 ± 0.12	16.86 ± 0.44
UMJ	1.13 ± 1.99	6.67 ± 2.75	3.44 ± 0.12	4.64 ± 0.09	7.48 ± 0.62	11.81 ± 0.1	14.55 ± 0.12	6.84 ± 0.18	2.04 ± 0.83	4.82 ± 1.13	1.52 ± 1.5	18.84 ± 0.5	19.06 ± 0.13
Site code (b)	HCB	HCH	HEPTA-CHLOR	ALDRIN	*o,p*-DDE	*p,p*-DDE	*o,p*-DDD	DIELDRIN	ENDRIN	*p,p*-DDD	*o,p*-DDT	*p,p*-DDT	MIREX
HND	0.38 ± 0.31	2.73 ± 0.16	2.83 ± 0.40	3.07 ± 0.38	0.58 ± 2.56	24.47 ± 0.12	3.63 ± 0.90	0.96 ± 0.08	1.45 ± 0.39	14.30 ± 0.12	1.55 ± 0.82	1.90 ± 1.36	15.13 ± 0.92
CMD	0.16 ± 0.58	2.57 ± 1.68	1.85 ± 0.66	0.45 ± 0.39	0.27 ± 1.78	7.49 ± 0.02	1.04 ± 0.19	0.82 ± 1.04	1.15 ± 0.16	6.84 ± 0.22	1.01 ± 1.74	0.71 ± 0.95	5.08 ± 0.21
DUT	0.1 ± 0.64	2.63 ± 0.00	2.12 ± 0.38	2.33 ± 0.35	1.57 ± 0.00	25.57 ± 0.03	5.81 ± 0.02	2.67 ± 0.36	1.60 ± 0.52	15.68 ± 0.00	0.08 ± 0.19	1.30 ± 0.44	11.95 ± 0.25
WWT 1	8.14 ± 0.16	16.08 ± 0.51	18.86 ± 0.07	19.59 ± 0.07	14.68 ± 0.26	40.47 ± 0.27	14.75 ± 0.46	18.99 ± 0.30	29.50 ± 0.39	81.15 ± 0.25	16.67 ± 1.42	36.19 ± 0.33	41.68 ± 0.55
WWT 2	2.66 ± 0.43	1.97 ± 0.29	3.66 ± 0.26	3.92 ± 0.25	5.98 ± 0.07	26.65 ± 0.14	5.68 ± 0.04	11.02 ± 0.54	4.05 ± 0.43	14.81 ± 0.20	4.84 ± 1.08	21.78 ± 0.6	11.46 ± 0.07
WWT 3	0.61 ± 1.86	2.77 ± 0.01	5.74 ± 0.25	6.06 ± 0.17	5.63 ± 0.02	28.35 ± 0.01	0.94 ± 0.46	4.9 ± 0.63	2.15 ± 0.09	10.60 ± 0.05	1.41 ± 0.39	6.08 ± 0.34	6.87 ± 0.14
AGA	0.05 ± 0.11	2.50 ± 0.12	0.37 ± 0.10	0.64 ± 0.43	2.76 ± 0.9	22.59 ± 0.02	3.22 ± 0.12	0.42 ± 2.22	2.01 ± 0.34	12.82 ± 0.05	1.71 ± 0.56	1.15 ± 0.28	7.86 ± 0.08
MST	4.67 ± 0.23	4.64 ± 0.2	9.13 ± 0.03	9.56 ± 0.03	3.08 ± 0.6	39.58 ± 0.12	12.84 ± 0.06	9.47 ± 0.17	5.66 ± 1.18	27.11 ± 0.01	1.53 ± 0.31	2.85 ± 0.61	23.66 ± 0.03
NGD	0.1 ± 0.64	5.52 ± 0.12	2.12 ± 0.38	1.79 ± 0.37	2.12 ± 0.06	25.57 ± 0.03	5.47 ± 0.15	1.75 ± 0.92	1.60 ± 0.52	15.24 ± 0.08	1.27 ± 0.01	1.19 ± 0.23	11.95 ± 0.25
UMJ	4.68 ± 0.24	5.60 ± 0.24	9.86 ± 0.76	10.32 ± 0.75	6.52 ± 0.18	36.33 ± 0.01	14.07 ± 0.08	12.28 ± 0.13	3.79 ± 0.66	24.42 ± 0.06	2.42 ± 1.37	5.10 ± 0.26	17.5 ± 0.11

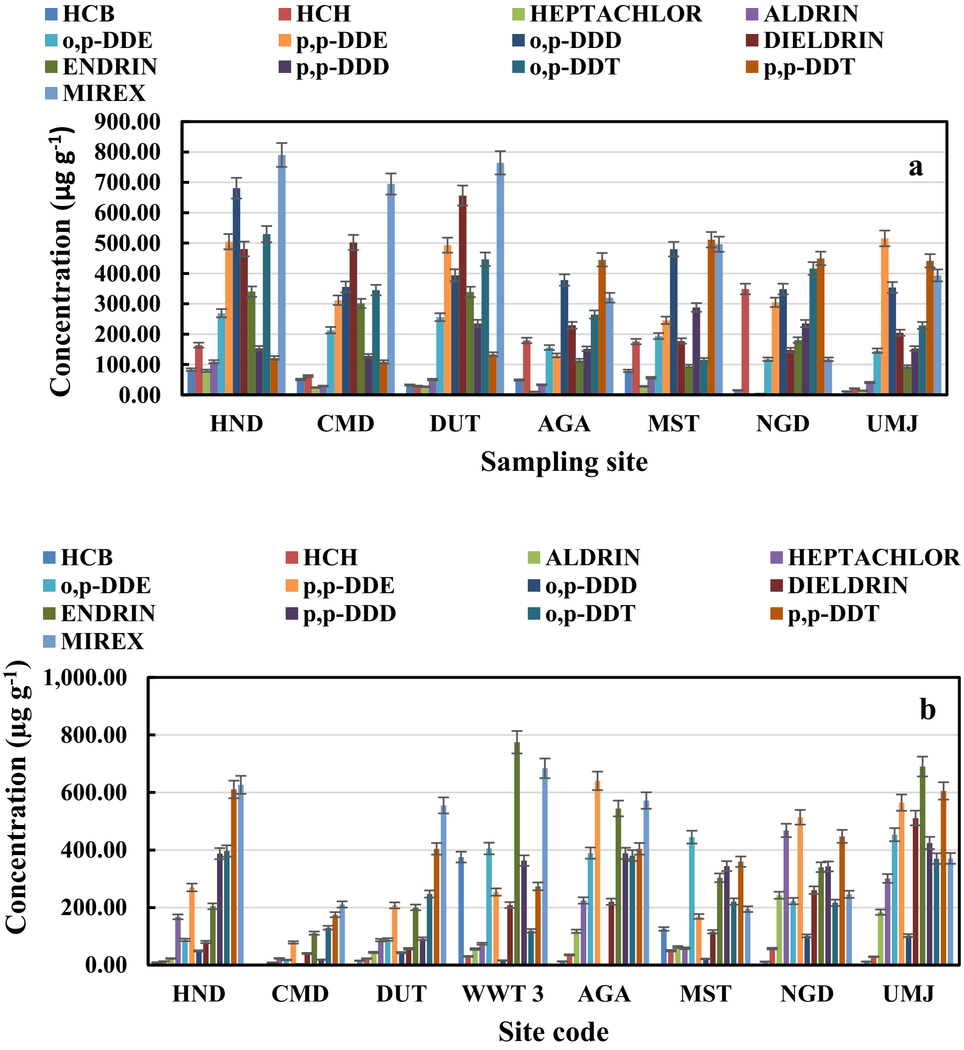

Fig. 4 Distribution of OCP concentrations in soil during **a** winter and **b** spring seasons along the sites

difference in concentrations during winter and spring seasons in water compared to sediment and soil. This could be attributed to the fact that mirex is very insoluble in water and binds strongly to the aquatic soil and sediment. Mirex has no natural origin but historically it has been used in South Africa as a termite control and produced industrially through catalytic processes of dimerization of hexachlorocyclopentadiene. It is also majorly used as an insecticide, flame retardant in plastics, paper and electrical appliances (ATSDR 1995; Ritter et al. 2005). Its production has since been banned, but the residues of this compound may still remain in the environment due to its long half-life, historical use, and accidental spillages, open dumping and burning and leaching from old materials. Both endrin and dieldrin (half-life of approximately 5 years in temperate soil for dieldrin) were also found in appreciable concentrations in the environmental media in both seasons and their source could possibly be traced to extensive usage in agriculture for the control of soil insect vectors of diseases before they were banned. Aldrin and heptachlor as well as HCH concentrations were lower compared to others, however the lower concentration of aldrin could possibly be due to its instability in the environment as aldrin is readily and rapidly converted to dieldrin (UNEP 2001; Ritter 2005). In this study, the indicative ratios of aldrin/dieldrin were 0.16, 0.37 and 0.14 in sediment, soil and water in winter and 0.94, 0.51, and 0.89 in the three matrices during spring, which confirms aldrin's degradation to dieldrin.

Generally, in this study, winter season was found to have the highest concentrations of nearly all the OCPs investigated. The trend could be attributed to the low water flow as well as low temperature during the winter season, which could possibly result into less dilution of OCPs in water and low aqueous solubility, and reduce the volatilization rate of the OCPs onto gas particle phase. Soil and sediment exhibited the highest OCP concentration during both seasons compared to surface water. The reason for this is that chlorinated pesticides have stronger carbon to chlorine bonds,

Table 4 Comparison of OCP concentration levels in sediment (ng g^{-1} dw), soil (ng g^{-1} dw) and water (ng mL^{-1}) with other studies

Location	ΣOCPs	Sediment (ng g^{-1})	Soil (ng g^{-1})	Water (ngmL^{-1})	References
Msunduzi River, South Africa	Σ^{13}OCPs	464.65–3773.66[a] 605.29–3534.97[b]	185.85–3576.91[a] 241.40–3460.71[b]	21.02–183.88[a] 21.55–277.07[b]	This study This study
Jukskei River, South Africa	Σ^{13}OCPs	4.26–22914		1.07–15400	Sibali et al. (2008)
Cocoa producing area, Ondo State, Nigeria	Σ^{15}OCPs	10-57400		1.07–15400	Okoya et al. (2013)
Qiantang River, China	Σ^{13}OCPs	23.11–316.50			Zhou et al. (2006)
Tasman,Waikato Auckland, New Zealand	Σ^{6}OCPs	30.0-34500			Gaw et al. (2006)
Agricultural Soils, India	Σ^{13}OCPs		3.59–160.30		Kumar et al. (2013)

dw Dry weight

[a] Winter

[b] Spring

which results in them having a lower affinity for water and higher tendency to bind to fatty tissue of organisms and particulate matter as well as soil humic substances having similar hydrophobic, lipophilicity characters and π–π interactions (WSPMP 1995; Ritter et al. 2005; Kumar et al. 2013).

The result of the present study in both river sediment and water was lower compared to the studies done by Sibali and co-workers, on the Jukskie River catchment area in Gauteng, South Africa (Sibali et al. 2008) and compared to sediment and water of a cocoa producing area in the Ondo State in Nigeria (Okoya et al. 2013) (Table 4). The study done by Gaw and co-workers on OCPs in sediments of Tasman Waikato Auckland, New Zealand was higher compared to the results obtained in this study even though they had only investigated 6 OCPs (Gaw et al. 2006). This study indicated that this particular river in South African is less polluted compared to some other parts of the world but is relatively contaminated compared to the study on the Qiantang River in China (Zhou et al. 2006) and the agricultural soils investigated in India (Kumar et al. 2013) (Table 4). Therefore, it is important to compare the results of other locations across the world that may have similar or different conditions from the current study, in terms of climate and weather conditions, geological information as well as hydrological characteristics. This is important to have clear understanding on the distribution pattern of the selected pollutants.

Conclusion

The concentrations of chlorinated pollutants were evaluated in sediment, soil and surface water samples during winter and spring seasons, from the Msunduzi River, South Africa. The pesticide concentrations were influenced by temperature during the studied seasons in the environmental media as well as the anthropogenic activities at the various sites. Among the sites sampled, apart from Darvill wastewater treatment plant influent with the highest OCP concentration, the Umgeni Msunduzi joining point and Du-Toit sites were also found to have higher concentrations of the selected pesticides. The results indicated that DDT and its metabolites were found to be more prevalent among the OCPs studied. This could probably be due to aged long weathering and anaerobic degradation of DDT isomers into their metabolites. The higher lipophilicity and particle affinity of DDT to sediments (low water solubility, high stability and semi-volatility) may also be a possible reason for the higher total concentrations of DDT obtained in this study despite their long time ban in South Africa. Total OCP concentrations in this present study were lower compared to that obtained in the Jukskei River catchment area in Gauteng, South Africa and generally higher than the tolerable level of 0.1 μg kg^{-1} guideline for aquatic ecosystems as recommended by the European Union (EU). Therefore, urgent attention and increased monitoring is required to protect the water ecosystem and health of people consuming this water.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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